(54) **RECOVERY OF METHACROLEIN AND/OR METHACRYLIC ACID, AND QUENCHING TOWER**
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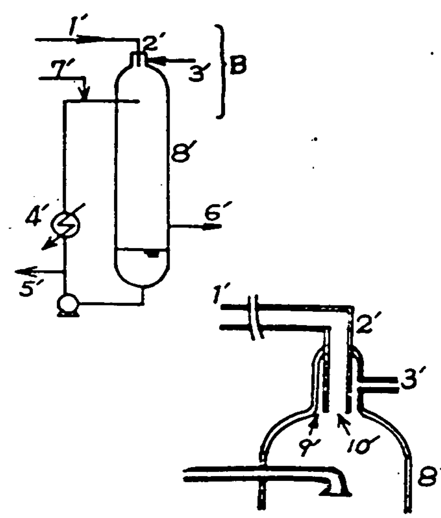

PURPOSE: To obtain the titled substance without troubles of e.g. blockage with high-boiling by-products, by introducing the reaction gas obtained by the vapor-phase oxidation of isobutylene, etc. into a quenching tower through an inlet maintained at high temp. at a flow rate higher than a specific level, and making parallel flow contact with the condensed liquid of the reaction gas.

CONSTITUTION: The reaction gas obtained by the vapor-phase oxidation of isobutylene, etc. is introduced through the pipes 1', 2' into the quenching tower 8', and quenched by the parallel flow contact with the condensed liquid cooled with the heat-exchanger 4' to obtain condensed liquid containing the titled substance and noncondensing gas. In the above procedure, the temp. of the inlet is maintained at ≧200℃ by the circular hot gas atmosphere sent through the hot gas introduction tube 3' and blasted from the hot gas nozzle 9', and the flow rate of the reaction gas at the inlet is maintained at ≧10m/sec.

EFFECT: By maintaining the inlet at high temp. and keeping the flow rate of the reaction gas at high level, the deposition of high-boiling by-product near the inlet can be prevented, and the operation can be continued for a long period. The generation of scum during the extraction can also be reduced.

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EUROPEAN PATENT APPLICATION

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(54) **Acrylic acid recovery with recycle quench.**

(57) Improved recovery of acrylic acid from a gaseous reactor effluent produced from the catalytic vapor phase oxidation of propylene or acrolein is accomplished by first quenching the reactor effluent, thereby forming vapor and liquid streams, indirectly cooling the vapor stream to condense a second liquid stream, and passing said second liquid stream to the quench system as the quench liquid.

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ACRYLIC ACID RECOVERY WITH RECYCLE QUENCH

BACKGROUND OF THE INVENTION

Acrylic acid is produced by the catalytic vapor phase oxidation of propylene or acrolein with molecular oxygen. Acrylic acid may be formed directly from acrolein using catalyst such as found in U.S. 3,736,354 and 3,644,509. Acrylic acid may also be formed from propylene in a one or two-stage operation. Although directed to the production of esters, U.S. 4,060,545 discloses catalyst that are effective to convert propylene directly to acrylic acid or to convert propylene to acrolein which is then reacted to acrylic acid. The catalyst used in these processes are known as activated oxide complexes.

The temperature of the reaction is typically between 300-600°C. The ratio of reactants may vary widely depending on whether propylene or acrolein is used as feed. Steam can be added to the reactor to increase selectivity of the catalyst. The reaction produces a gaseous reactor

effluent containing acrylic acid, acrolein, water and various impurities. These impurities consist of such components as acetic acid and inert gases.

In order to effectively recover acrylic acid, it is first necessary to obtain the acrylic acid in an aqueous solution suitable for later purification. The prior art has attempted this in a variety of ways. As described in the prior art section of U.S. 3,926,744, the gaseous reactor effluent is first cooled by using a liquid which is obtained by recycling cooled constituents of the condensate from this first step as a quenching liquid. This process has several disadvantages in that polymers deposit in the equipment, and the equipment size must be relatively large to handle both the quench liquid and the aqueous solution of acrylic acid.

The above reference presents another solution to the formation of an aqueous acrylic acid solution by utilizing organic materials such as hexyl alcohol in the quench system to decrease the formation of polymers and aid in the separation of acrolein.

U.S. 3,717,675 discloses a process wherein the reaction gas is first indirectly cooled to a temperature of 100-200°C, and the pre-cooled gases are then scrubbed with water to a temperature between 30° and 90°C. This process suffers from the disadvantage of requiring an extremely large indirect heat exchanger to handle the total gaseous reactor effluent.

The present invention reduces the size of equipment involved, and improves the recovery of acrylic acid from the gaseous reactor effluent by means of a unique quench recycle.

SUMMARY OF THE INVENTION

It has been discovered that the recovery of acrylic acid can be improved in the process for the recovery of acrylic acid from a gaseous reactor effluent containing acrylic acid, acrolein, water and impurities produced from the catalytic vapor phase oxidation of propylene or acrolein comprising the steps of:

a) quenching the gaseous reactor effluent with a quench liquid wherein a first liquid stream containing acrylic acid and a first vapor stream containing acrylic acid are formed;

b) indirectly cooling said first vapor stream to form a second liquid stream containing acrylic acid and a second vapor stream;

c) passing said second liquid stream as the quench liquid of step (a).

Within the scope of the invention are also included the steps of:

d) passing the second vapor stream to a scrubber utilizing water, wherein a third vapor stream containing uncondensed gases is removed overhead and a third liquid stream is removed from the bottoms; and

e) combining said third liquid stream with said first vapor stream prior to the indirect cooling of step (b).

This embodiment of the invention provides for the near total recovery of acrylic acid from the gaseous reactor effluent by combining the bottoms stream from the scrubber with the first vapor stream produced from the quench system.

The invention may be best understood by reference to the drawings.

DESCRIPTION OF THE DRAWINGS

Figure 1 shows the prior art method of obtaining an queous acrylic acid solution for further purification.

Figure 2 shows an embodiment of the present invention utilizing the recycle quench.

Figure 3 discloses a unique embodiment wherein all the steps necessary to obtain the aqueous acrylic acid solution are performed in one column.

Referring to Figure 1, the gaseous reactor effluent 1 is passed to quench column 2. The purpose of this column is to cool the gaseous reactor effluent and condense the acrylic acid. Quenching liquid is provided through line 4 and is sprayed countercurrent with the reactor effluent stream. The condensed acrylic acid and water are removed

from the quench column through line 6, indirectly cooled in exchanger 8, and then split into two streams. A portion is passed through line 4 as quench liquid previously described, and an aqueous solution of acrylic acid is removed through line 10 and passed to further recovery and purification (not shown). The vapor stream 12 removed from the quench column overhead typically contains acrylic acid, acrolein, inert gases and impurities. This is passed to an absorber 14. Water enters the absorber overhead through line 16 at a temperature sufficient to absorb the acrolein and thus allow a liquid stream 18 containing acrolein to be removed from the bottoms of the absorber and passed to further purification. The inert gases are removed overhead from the absorber through line 20. As can be noted from this drawing, not all of the acrylic acid is recovered in the quench column. A portion is removed in the gaseous overhead stream and exits the system with the acrolein from the bottoms of the absorber. Further, the total stream of quench liquid plus the aqueous acrylic acid product is cooled through exchanger 8, resulting in large capital investment for exchanger

Figure 2 shows an embodiment of the present invention utilizing recycle quench. The reactor effluent is passed through line 32, combined with quenching liquid 34, and passed to quench separator 36. As shown in this figure, the quenching occurs with cocurrent contact prior to the

entry into the separator. The quenching may also be counter-current within the separator as shown in Figure 1. In the separator 36, the aqueous acrylic acid solution is removed as a bottoms stream through line 38, with the remaining vapors passing overhead through line 40. These vapors are then cooled indirectly in heat exchanger 42. Prior to their entry into the heat exchanger, a recycle stream 44 can be combined with these vapors.

The vapors are then partially condensed in exchanger 42 through the use of cooling water. The bottommost section 46, of exchanger 42, serves as a separator. The condensed liquid containing acrylic acid is passed through line 34 as the quench liquid. The vapors are sent through line 48 to scrubber 50.

The purpose of scrubber 50 is to remove the uncondensible gases and acrolein, and to recover any remaining acrylic acid. Water is passed to scrubber 50 through line 52. The inert gases containing some acrolein is removed overhead through line 54, and a liquid bottoms stream containing acrylic acid is removed through line 44. This stream can either be combined with the vapors removed from the quench system as shown by the solid line, or can be combined directly with the quench liquid in 34 as shown by the dotted line 44 a.

Figure 3 shows an embodiment of the invention wherein all the processing steps are combined in one column. The reactor effluent is sent through line 60 to the bottom-most portion of the column 62. Above section 62 is the adiabatic section 64. Liquid falling from the cooling section above cools the reactor effluent thus condensing acrylic acid. In cooling section 66, liquid is removed from a side tray through line 68. This liquid is cooled in exchanger 70 and is recycled back to the cooling section through line 72 and sprayed countercurrent with the up-flowing gases. This produces the liquid necessary for recycle and for quench.

The remaining uncondensed gases then pass through absorption section 74. Water enters the top of this section through line 76 and operates in the same manner as the absorber shown in Figure 2. The uncondensed gases with acrolein are removed overhead through line 78, and the condensed liquid falls into cooling section 66 with the condensed acrylic acid cascading down the tower. Finally, the aqueous solution of acrylic acid is removed through line 80 and passed to further recovery and purification.

The use of such a quench allows for excellent recovery of acrylic acid, improves the elimination of low boiling reaction products, and has no need for refrigeration as found in the prior art. The cooling of the reactor effluent to condense acrylic acid is accomplished by evaporation of the quench liquid. The reactor effluent thus drops in temperature to its saturation temperature at its operat-

ing pressure. The operating temperatures and pressures vary depending on whether propylene or acrolein is used as a feed. The pressure of such systems are well known in the art and usually between 2 and 10 psig while the reactor effluent temperature is usually between 300 and 600°C. The adiabatic quench usually operates at temperatures above 70°C.

The quenching of the reactor effluent may be cocurrent or countercurrent, with co-current being preferred. As shown in Figure 2, quenching may take place in an expanded portion of the reactor effluent line prior to its entry into the quench separator. The quench is sprayed co-currently with the flow of the gases. However, quenching may also be provided countercurrently with spray nozzles at the top of the quench separator as known in the prior art.

The gases from the quench separator are then indirectly cooled in a shell and tube heat exchanger. Typically cooling water is used as a cooling medium. Because of the adiabatic nature of the quench, no refrigeration is necessary for the operation of this process. No refrigeration is required because a scrubber is used to enhance acrylic acid recovery. Other processes, known in the art use a refrigerated quench section to improve recovery efficiency.

The indirect cooling achieves partial condensation of the remaining gaseous stream. The liquid resulting from this condensation, at a temperature of approximately 40°C (again depending upon the pressure) is then used as the quench liquid described previously. By obtaining the quench liquid in this manner, polymerization is greatly reduced as is the need for external cooling.

The vapors resulting from the indirect cooling can then be passed to a gas scrubber. The purpose of this scrubber is to remove uncondensible gases and acrolein from the remaining acrylic acid and water. Water is fed to the scrubber at a water/feed ratio of between 0.05 and 0.15 by wt. with 0.075 being preferred. The operating temperature of this water is approximately 40°C but can range between 32°C and 45°C. At 40°C, no external refrigeration is necessary. The number of trays found in the scrubber will of course be a function of the feed composition and the amount and temperature of the water used to scrub. Typically this column consists of about 15 trays, with the feed entering below the first tray. Acrylic acid and water are recovered in the bottoms of the scrubber.

For total recovery purposes, this stream can be recycled to one of two locations. It can be combined with the vapors from the quench system prior to indirect cooling, or it can be combined directly with the quench liquid recovered from the indirect cooling that is sent to the quench system. Thus excellent recovery of acrylic acid can be obtained through using the present invention.

The aqueous acrylic acid solution recovered from the present invention is passed to further recovery and purification. Such purification is known in the art and can be found in U.S. 3,830,707, U.S. 3,859,175 and U.S. 3,433,831. These patents disclose various processes such as extraction or entrainment with various solvents to separate acrylic acid into final product purity.

EXAMPLE

A gaseous reactor effluent stream produced from the vapor phase oxidation of proyplene, and containing 50% acrylic acid with the remainder being acetic acid, acrolein, water, and gases such as nitrogen and carbon dioxide, were passed to the invention's quench system. The quench system consisted of a 12' long quench column containing 5 spray nozzles for cocurrent quenching and having a quench pot located at the bottoms of the column for separating the vapor from the liquid phase. Reactor effluent entered the quench column at a temperature of 200°C. All liquid recovered from the indirect heat exchanger, containing approximately 38% acrylic acid, was passed to the quench column spray nozzles.

After quenching, the liquid was separated from the vapors. The aqueous solution removed from the separator contained on the average, 60 wt.% acrylic acid. The quench column vapors at a temperature of 79°C were then passed to

an 8" vertical shell and tube heat exchanger with a spray section above it and a separation pot below. To simulate a 3-cycle bottoms stream, water containing acrylic acid was passed to the spray section prior to the indirect heat exchange.

Cooling water was used on the shell side of the exchanger to cool the gases to a temperature of 40°C. The phases were then separated, with the quench liquid containing approximately 38% acrylic acid and the gases containing approximately 1 to 2% acrylic acid .

Without the operation of a scrubber to recover the remaining acrylic acid, the invention's quench system with the indirect exchanger allows for an 88% recovery efficiency of acrylic acid. The addition of a scrubber column will allow near complete recovery to be accomplished.

I CLAIM:

1. In the process for the recovery of acrylic acid from a gaseous reactor effluent containing acrylic acid, acrolein, water and impurities produced from the catalytic vapor phase oxidation of propylene or acrolein comprising the steps of:

a) quenching the gaseous reactor effluent with a quench liquid wherein a first liquid stream containing acrylic acid and a first vapor stream containing acrylic acid are formed;

b) indirectly cooling said first vapor stream to form a second liquid stream containing acrylic acid and a second vapor stream and

c) passing said second liquid stream as the quench liquid of step (a).

2. The process of claim 1 wherein the quenching of the gaseous reactor effluent is accomplished co-currently.

3. The process of claim 1 wherein the reactor effluent is quenched to a temperature of between 70 and 90°C.

4. The process of claim 1 wherein the feed is propylene.

5. The process of claim 1 including the additional steps of:

d) passing said second vapor stream to a scrubber utilizing water, wherein a third vapor stream containing uncondensed gases is removed overhead and a third liquid stream containing acrylic acid is removed from the bottoms.

6. The process of claim 5 wherein the water/feed ratio of the scrubber is between 0.05 and 0.10.

7. The process of claim 6 wherein the scrubber contains between 10 to about 20 absorption trays.

8. The process of claim 5 including the step of combining said third liquid stream with said first vapor stream prior to the indirect cooling of step (b).

9. The process of claim 5 including the step of combining said third liquid stream with said second liquid stream of step (b) and passing the combined streams as the quench liquid of step (a).

10. In the process for the recovery of acrylic acid from a gaseous reactor effluent containing acrylic acid, acrolein, water and impurities produced from the catalytic vapor phase oxidation of propylene or acrolein in a single column having a quenching, cooling and absorbing section, comprising the steps of:

a) quenching the reactor effluent with a quench liquid from the cooling section;

b) directly cooling said quenched reactor effluent with a cooling medium to condense a portion of said effluent,

c) indirectly cooling said condensed effluent prior to the direct cooling;

d) absorbing the acrylic acid in an absorbing section by contacting the quenched, cooled reactor effluent with water;

e) removing an aqueous solution containing acrylic acid from the bottoms of said column.

0009545

Application number

European Patent Office

EUROPEAN SEARCH REPORT

EP 79 102 324.5

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	GB - A - 1 466 209 (CELANESE) * claim 1 *	1
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A,D	US - A - 3 717 675 (K. SENNEWALD et al.) * claim 1 *	1
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A	GB - A - 1 293 848 (TOYO SODA) * claim 1 *	1

CLASSIFICATION OF THE APPLICATION (Int. Cl.3)

C 07 C 57/04
C 07 C 51/42
B 01 D 5/00

TECHNICAL FIELDS SEARCHED (Int.Cl.3)

B 01 D 5/00
C 07 C 51/42
C 07 C 57/04

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Berlin	19-12-1979	KNAACK

FIG. 1
(PRIOR ART)

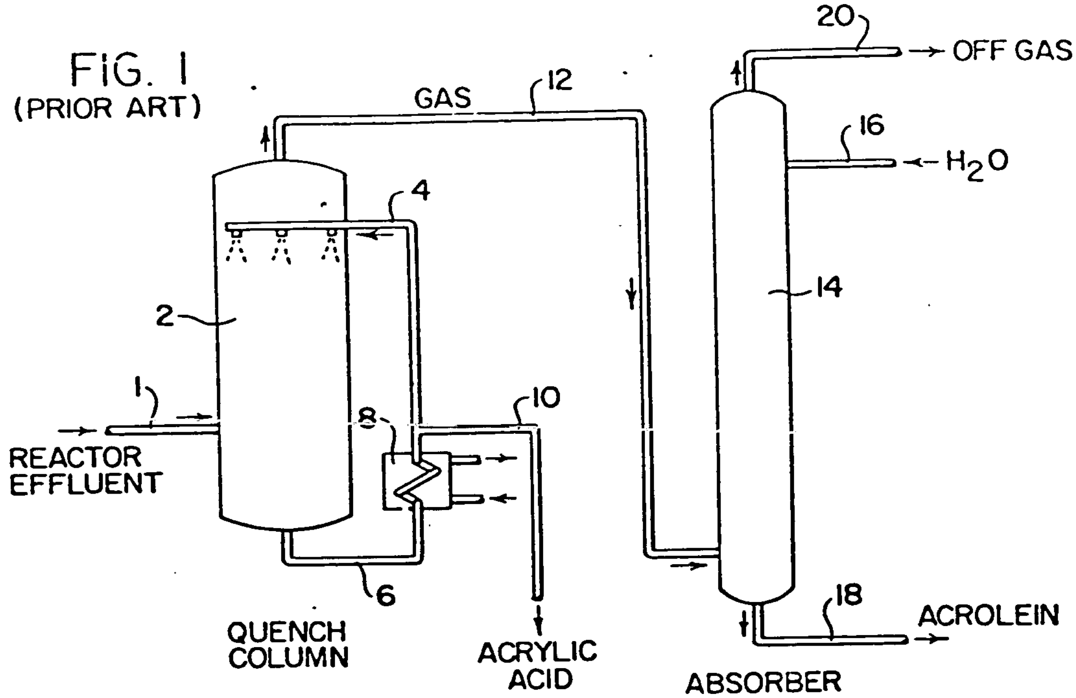


FIG. 2

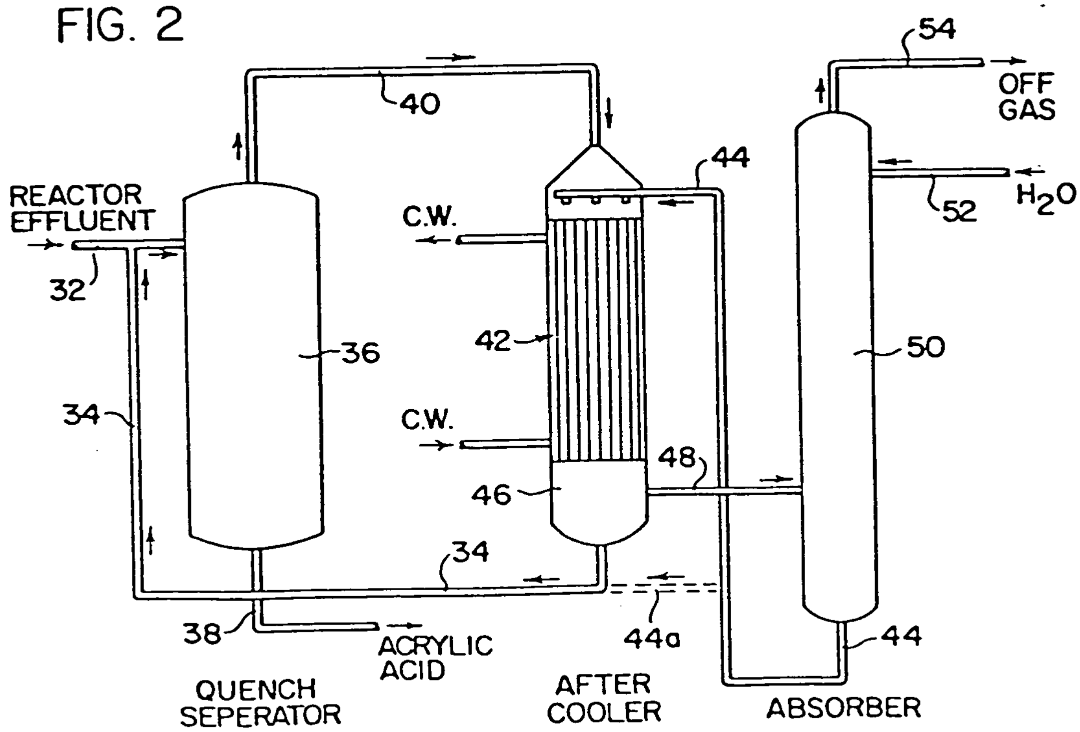
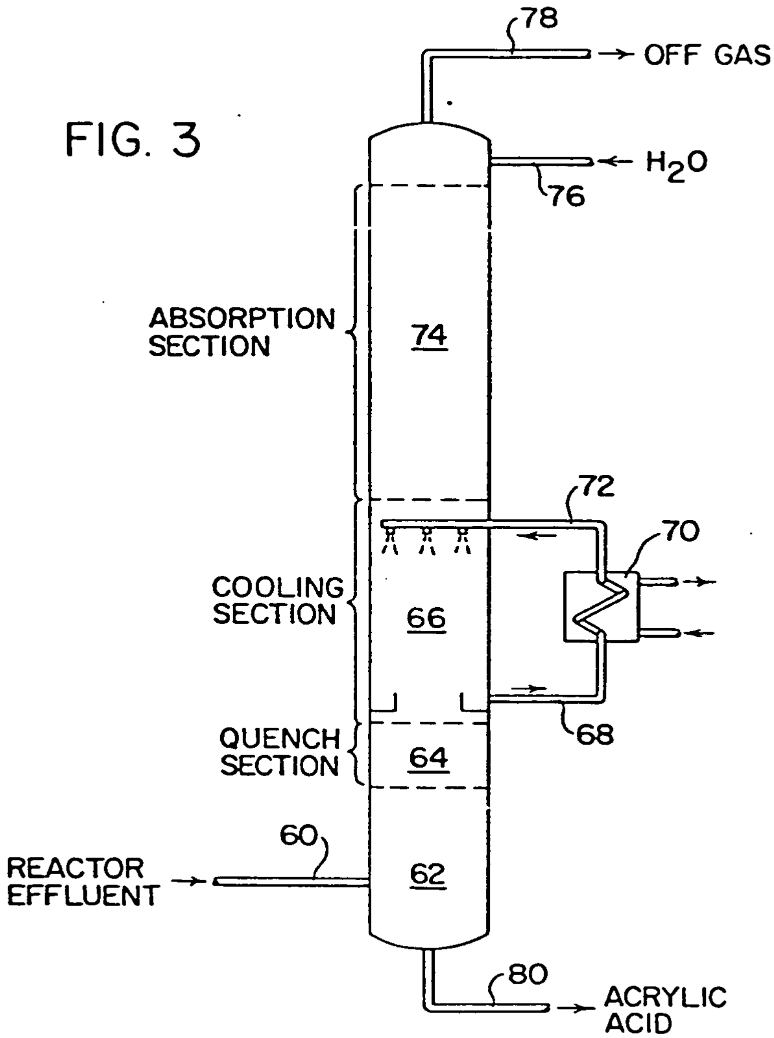


FIG. 3


78
OFF GAS
H_2O
76
ABSORPTION SECTION
74
72
70
COOLING SECTION
66
68
QUENCH SECTION
64
60
REACTOR EFFLUENT
62
80
ACRYLIC ACID